Bent Metallocenes of Germanium, Tin, and Lead with Aminoboratabenzene Ligands − Crystal Structures of $E[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$ (E = Ge, Sn, and Pb)[‡]

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Keywords: Boron / Metallocenes / Sandwich compounds / Germanium / Tin / Lead

The reaction of GeI_2, $SnCl_2$, or $PbCl_2$ with two equivalents of lithium aminoboratabenzenes in diethyl ether affords the new sandwich compounds $Pb(3,5\text{-}Me_2C_5H_3BNMe_2)_2$ (**4**) and $E[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$ (**5:** E = Ge, **6:** E = Sn, **7:** E = Pb). While compound **4** undergoes a redox ligand coupling reaction at ambient temperature to give lead black and ligand dimers, the bis(trimethylsilyl)amino compounds **5**–**7** are thermally stable, and coupling products are only detected under the conditions of mass spectrometry. This difference in stability can be attributed to the different perturbation effects which the *B*-amino groups exert on the electronic properties of the boratabenzene rings. Crystal structure determinations reveal that the compounds **5**–**7** possess a monomeric bent-sandwich geometry in the solid state with facially bonded boratabenzenes. The E–C distances span rather large ranges [**5:** 2.320–2.939(4) Å; **6:** 2.519–3.033(9) Å; **7:** 2.632–3.054(7) Å]; the central element E is always particularly close to one of the two α-C atoms and displays intermediate E–B distances.

Introduction

Compared to sandwich complexes of the transition metals, group 14 metallocenes exhibit a more ionic bonding character of the metal−ligand interactions and minimal involvement of the metal d orbitals. These features give rise to loose electronic demands and flexible bonding situations, which have well been documented in recent years with the observation of great structural diversity in this family of compounds.[1−3]

In the solid state, group 14 metallocenes can essentially be classified into three types (Figure 1). Bridging μ-η^5:η^5 cyclopentadienyl ligands (type **A**) exist in all three polymorphic modifications of the parent plumbocene, $Pb(C_5H_5)_2$, with the structural motifs of a zigzag chain,[4] of a toluene/solvated sinusoidal chain,[5] and of a hexameric aggregate.[5] Utilization of lighter homologues[6,7] and/or of sterically demanding cyclopentadienyl ligands[8−10] affords the most frequently encountered bent sandwich structures (type **B**);[1] in some cases, extra short intermolecular interactions are present among neighboring molecules in the lattice.[11] Finally, high steric congestion may cause a parallel alignment of the two cyclopentadienyl rings, resulting in a linear sandwich geometry (type **C**).[12−15] The first group 14 metallocene with parallel ring ligands to be discovered was decaphenylstannocene $Sn(C_5Ph_5)_2$,[12] and the first linear germanocene and plumbocene were $E[(C_5Me_4(SiMe_2tBu)]_2$ (E = Ge, Pb).[13] Interestingly, in the case of decamethylsilicocene $Si(C_5Me_5)_2$ two independent isomers are observed in the crystal structure, one with parallel pentamethylcyclopentadienyl ligands and the other one with a bent geometry.[16]

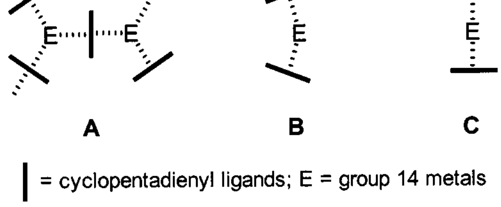

Figure 1. Three structural types of group 14 metallocenes

As aromatic anionic ligands with some similarity to cyclopentadienides, boratabenzenes have drawn substantial research interest recently.[17,18] However, boratabenzene compounds of p-block elements are still quite rare.[19−22] In previous work, we have synthesized the bis(1-methylboratabenzene) compounds $E(C_5H_5BMe)_2$ (**1**: E = Ge; **2**: E = Sn; **3**: E = Pb).[19] X-ray diffraction studies showed that the lead compound **3** possesses a bent geometry locally and forms a tetrameric packing aggregate with short intermolecular contacts which indicate a specific interaction between the lead atoms and the most negatively charged α-carbons of the boratabenzenes of neighboring molecules. In this paper, we describe the synthesis and characterization of the bis(aminoboratabenzene) compounds **4**−**7** using 1-(dimethylamino)-3,5-dimethylboratabenzene and 1-[bis(trimethylsilyl)amino]-3,5-dimethylboratabenzene as ligands. A comparison of their spectroscopic and structural data with those of the known 1-methylboratabenzene analogues provides insight into the electronic and steric effects of the *B*-bonded substituents on group 14 metal−boratabenzene complexes.

[‡] Borabenzene Derivatives, 36. − Part 35: X. Zheng, G. E. Herberich, *Organometallics* **2001**, *20*, 3097−3100.

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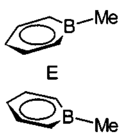
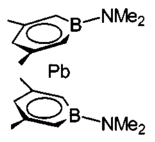


1: E = Ge
2: E = Sn
3: E = Pb



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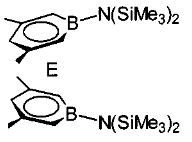

5: E = Ge
6: E = Sn
7: E = Pb

Results and Discussion

Syntheses

Salt-metathetical reactions were used in the present work to synthesize the bis(aminoboratabenzene) compounds of the group 14 elements. We had previously reported the synthesis of $Pb(C_5H_5BMe)_2$ (**3**) from lithium 1-methylboratabenzene and $PbCl_2$ in a 2:1 molar ratio.[19] The analogous reaction of lithium 1-(dimethylamino)-3,5-dimethylboratabenzene with $PbCl_2$ at −30 °C produced $Pb(3,5\text{-}Me_2C_5H_3BNMe_2)_2$ (**4**) as a red oil. The formation of the targeted compound was verified by ^1H, ^{11}B, and ^{13}C NMR spectroscopy. Unfortunately, **4** is thermally unstable at ambient temperature and decomposes completely within hours to give lead black as well as an oily mixture of ligand coupling products. To avoid thermal decomposition, all manipulations must be performed at temperatures lower than −20 °C. A similar oxidative coupling reaction had previously been observed when a pinene-fused aminoboratabenzene ion was treated with CuI.[23]

The different stabilities of **3** and **4** seem to arise from the different electronic perturbations of the *B*-amino substituents on the boratabenzene ligands.[24−27] In general, considerable π-interactions exist between the nitrogen and the boron for 1-(dialkylamino)boratabenzenes.[24] This B−N π-interaction is antibonding with respect to the intra-ring B−C π-conjugation, which consequently makes aminoboratabenzenes somewhat similar to the open pentadienyl ligand.[25] Using cyclopentadienide ions as reference, Ashe et al.[26] evaluated the pK_a values of several boracyclohexadienes (or dihydroborinines), the conjugate acids of the corresponding boratabenzene ions, in DMSO by means of NMR spectroscopic methods. The pK_a of 1-methylboracyclohexa-2,5-diene is lower than 12.5 whereas that of 1-(diisopropylamino)boracyclohexa-2,5-diene reaches 17.8 (cf. $pK_a = 18.0$ for CpH[28]). In other words, 1-(dimethylamino)boratabenzene is considerably more basic than 1-methylboratabenzene, and hence should be more prone to oxidation and oxidative ligand coupling.

We then chose 1-[bis(trimethylsilyl)amino]-3,5-dimethylboratabenzene as the ligand. From the viewpoint of electronic effects, the polarizing positive Si centers stabilize the nitrogen lone-pair and weaken the B−N π-conjugation; as a consequence, this ligand is expected to be less basic and less nucleophilic than the *B*-(dimethyamino) analogue. The reduced π-conjugation is evidenced by the B−N bond length in the crystal structure of $ScCl[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$ [1.471(3) Å] which is considerably longer than that of the η^6-bonded 1-(dialkylamino) ligand in $[ScCl(3,5\text{-}Me_2C_5H_3BNMe_2)]_2$ [1.417(3) Å].[29] Further support comes from the ^{11}B NMR spectroscopic data of the relevant compounds as will be discussed in some detail below. From the viewpoint of steric effects, the bulky *B*-bis(trimethylsilyl)amino substituent of the ligand is expected to enhance the kinetic stability of its complexes.

The bis[1-bis(trimethylsilyl)amino-3,5-dimethylboratabenzene] compounds **5**−**7** can be obtained in good yields (63−85%) from a suitable dihalide (GeI_2, $SnCl_2$, or $PbCl_2$) and 2 equivalents of $Li[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]$ using diethyl ether as the solvent. All three compounds can be crystallized from pentane at −30 °C as large prisms. Since the previously known 1-methyl compounds **1** and **2** are liquids, the new compounds **5** and **6** of germanium and tin are the first crystalline bis(boratabenzene) derivatives of these elements. While **5** and **6** are pale yellow, the lead compound **7** is orange red; they are thermally stable at room temperature but quite sensitive to moisture and oxygen.

Spectroscopic Data

The new compounds were characterized by multinuclear NMR spectroscopy and electron-impact mass spectrometry (EIMS). The ^{11}B NMR chemical shifts for **1**−**7** are collected in Table 1, together with data for the related lithium boratabenzenes. On going from germanium to lead, the chemical shifts $\delta(^{11}B)$ move to high field and are, for the lead−boratabenzene compounds, very close to the chemical shifts of the corresponding lithium boratabenzenes.[29,30] This increase (**5** < **6** < **7**) indicates an increasing electrostatic contribution to the metal−ligand interactions for the heavier homologues, which reduces the transfer of electron density from the ligand to the cationic center. Moreover, a survey of the ^{11}B NMR spectroscopic data also provides an insight into the influence of the *B*-bonded substituents on the electronic properties of the ligands. In the case of 1-[bis(trimethylsilyl)amino]-3,5-dimethylboratabenzene, the polarizing influence of the positive silicon centers, as well as the steric demand of the *B*-substituent, diminishes the π-interaction in the B−N bond.[29] Therefore, the ^{11}B chemical shifts of its compounds are located between those of

Table 1. ^{11}B NMR chemical shift data for **1**−**7**[a]

Compound	$\delta(^{11}B)$	ref.
$Ge(C_5H_5BMe)_2$ (**1**)	41	[19]
$Sn(C_5H_5BMe)_2$ (**2**)	38	[19]
$Pb(C_5H_5BMe)_2$ (**3**)	36.1	[19]
$Li(C_5H_5BMe)_2$	36	[30]
$Ge[Me_2C_5H_3BN(SiMe_3)_2]_2$ (**5**)	37.8	this work
$Sn[Me_2C_5H_3BN(SiMe_3)_2]_2$ (**6**)	36.3	this work
$Pb[Me_2C_5H_3BN(SiMe_3)_2]_2$ (**7**)	35.2	this work
$Li[Me_2C_5H_3BN(SiMe_3)_2]$	34.5	[29]
$Pb(Me_2C_5H_3BNMe_2)_2$ (**4**)	32	this work
$Li(Me_2C_5H_3BNMe_2)$	31.6	[29]

[a] Chemical shifts were measured in CD_2Cl_2 for group 14 metal compounds and in $[D_8]THF$ for lithium boratabenzenes.

the 1-methylboratabenzene and those of the 1-(dimethylamino)-3,5-dimethylboratabenzene compounds.

The ^{119}Sn and ^{207}Pb NMR chemical shifts for the relevant compounds are listed in Table 2. $\delta(^{119}Sn)$ for **6** is located at $\delta = -1592$ and the $\delta(^{207}Pb)$ for **7** at $\delta = -2890$. Both values are slightly more negative than those of the 1-methylboratabenzene analogues [**2**: $\delta(^{119}Sn) = -1535$, **3**: $\delta(^{207}Pb) = -2579$],[19] and far less negative than those of the cyclopentadienyl analogues [e.g., $Sn(C_5H_5)_2$:[31] $\delta(^{119}Sn) = -2199$, $Pb(C_5H_5)_2$:[32] $\delta(^{207}Pb) = -5030$].[34] As discussed in our earlier paper, these dramatic differences can qualitatively be related to the different donor properties of the ligand anions (mainly influencing σ_{dia}) and to the different HOMO/LUMO gaps (influencing σ_{para}).[19]

The EIMS data for **5−7** are summarized in Table 3. All three compounds exhibit very weak parent peaks $\{[EL_2 - 1]^+$, $I_{rel} < 1\%$; E = Ge, Sn, Pb; L = $3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2\}$ and feature two sequential losses of the boratabenzene ligands. The most abundant peaks belong to the cations EL^+ or L^+. It is interesting to note that the fragments L_2^+ and $[L_2 - Me]^+$ are also present in the mass spectra. This observation indicates that oxidative ligand coupling reactions are taking place under the conditions of mass spectrometry.

Table 2. ^{119}Sn and ^{207}Pb NMR chemical shift data

Compound	$\delta(^{119}Sn)$	$\delta(^{207}Pb)$
$E(C_5H_5BMe)_2$ (**2** and **3**)	−1535[19]	−2584[19]
$E[Me_2C_5H_3BN(SiMe_3)_2]_2$ (**6** and **7**)	−1592	−2890
$E(C_5H_5)_2$	−2199[31]	−5030[32]
$E(C_5Me_5)_2$	−2121[33]	−4390[32]
$E[(C_5Me_4(SiMe_2Bu\textit{t})]_2$	−2204[13c]	−4595[13c]
$E(C_5Ph_5)_2$ [a]	−2215[32]	−6150[32]

[a] Chemical shifts were measured in the solid state.

Table 3. Mass spectroscopic data for **5−7**[a]

Fragment	m/z (I_{rel} [%]) **5** (E = Ge)	 **6** (E = Sn)	 **7** (E = Pb)
$[EL_{2-}1]^+$	602 (< 1)	647 (< 1)	735 (< 1)
L_2^+	528 (1)	528 (2)	528 (20)
$[L_2 - Me]^+$	513 (1)	513 (13)	513 (80)
EL^+	338 (100)	384 (100)	472 (30)
L^+	264 (30)	264 (48)	264 (100)
E^+	74 (3)	120 (4)	208 (1)

[a] E = Ge, Sn, Pb; L = $[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]$.

Crystal Structures of $E[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]_2$ (E = Ge, Sn, Pb)

The crystal structures of the compounds **5−7** were determined by X-ray diffraction methods (Table 4 and 5). The germanium compound **5** (Figure 2) crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$) whereas the tin compound **6** and the lead compound **7** (both with an overall structure very similar to that of **5** and therefore not shown) adopt the triclinic space group $P\bar{1}$ ($Z = 4$) with two independent, but quite similar molecules per asymmetric unit. The latter two compounds are isomorphous in the solid state.

All three structures are of a bent-sandwich type, and no specific intermolecular interactions between neighboring molecules are observed. The two boratabenzene ligands are orientated in such a way that the two voluminous bis(trimethylsilyl)amino groups are related to each other with rotational angles of 147−162° so as to minimize repulsive interactions. The B−N bond lengths [1.46−1.49(1) Å] are comparatively long, and the interplanar angles between the best boratabenzene C_5B plane and the amino NSi_2 plane are quite large. Both observations indicate rather weak π-interactions between the boron and the nitrogen.

The central elements display a rather asymmetric bonding to the boratabenzene rings. This is evidenced by the fact that the metal-to-carbon/boron distances span a very large range, especially in the case of the germanium compound [**5**: 2.320−2.939(4) Å; **6**: 2.519−3.033(9) Å, **7**: 2.632−3.054(7) Å]. Note that the E−B distances are even slightly shorter than some of the E−C distances despite the larger covalent radius of the boron atom. In such a situation, a statement about ligand hapticity would seem quite arbitrary, but we may safely state that the ligand is facially coordinated to the central element.

Table 4. Selected bond lengths (Å) for **5−7**

5		**6**				**7**			
Ge−C12	2.321(4)	Sn1−C12	2.540(9)	Sn2−C32	2.534(8)	Pb1−C12	2.644(6)	Pb2−C32	2.632(6)
Ge−C13	2.467(4)	Sn1−C13	2.616(10)	Sn2−C33	2.634(9)	Pb1−C13	2.706(7)	Pb2−C33	2.702(7)
Ge−C14	2.637(4)	Sn1−C14	2.783(9)	Sn2−C34	2.784(10)	Pb1−C14	2.853(7)	Pb2−C34	2.862(6)
Ge−C15	2.913(4)	Sn1−C15	3.024(8)	Sn2−C35	3.027(9)	Pb1−C15	3.034(6)	Pb2−C35	3.043(6)
Ge−C16	2.939(4)	Sn1−C16	3.017(8)	Sn2−C36	3.030(9)	Pb1−C16	3.049(6)	Pb2−C36	3.046(7)
Ge−B1	2.739(5)	Sn1−B1	2.898(9)	Sn2−B3	2.914(9)	Pb1−B1	2.973(7)	Pb2−B3	2.953(7)
Ge−C22	2.320(4)	Sn1−C22	2.530(8)	Sn2−C42	2.519(9)	Pb1−C22	2.642(6)	Pb2−C42	2.634(6)
Ge−C23	2.454(4)	Sn1−C23	2.620(9)	Sn2−C43	2.624(10)	Pb1−C23	2.704(7)	Pb2−C43	2.714(7)
Ge−C24	2.612(4)	Sn1−C24	2.787(9)	Sn2−C44	2.787(10)	Pb1−C24	2.851(7)	Pb2−C44	2.840(6)
Ge−C25	2.874(4)	Sn1−C25	3.008(9)	Sn2−C45	3.029(9)	Pb1−C25	3.047(6)	Pb2−C45	3.040(7)
Ge−C26	2.908(4)	Sn1−C26	3.033(8)	Sn2−C46	3.013(9)	Pb1−C26	3.049(6)	Pb2−C46	3.054(7)
Ge−B2	2.736(5)	Sn1−B2	2.907(9)	Sn2−B4	2.907(9)	Pb1−B2	2.968(7)	Pb2−B4	2.948(7)
N1−B1	1.486(6)	N1−B1	1.464(12)	N3−B3	1.476(12)	N1−B1	1.480(9)	N3−B3	1.481(8)
N2−B2	1.474(6)	N2−B2	1.458(12)	N4−B4	1.494(11)	N2−B2	1.466(9)	N4−B4	1.486(8)

Table 5. Structural data related to the best least-squares planes for **5**−**7**[a]

Compound	**5**	**6**	**7**
Max. deviation from C_5B planes [Å]	0.072 (C*n*2)	0.055 (C*n*2)	0.047 (C*n*2)
Tilt angle of the sandwich unit [°]	43	51	51
Metal distance to best C_5B plane [Å]	2.179	2.375	2.456
Rotational angle between ligands[b] [°]	162	148	147
Slip distortion[c] [Å]	0.56	0.51	0.43

[a] The data are averaged where applicable. − [b] The rotational angle of the two boratabenzene ligands A and B is defined as the angle between the projections of the two exocyclic B−N bond vectors onto the C_5B plane of the ligand A. − [c] The slip distortion is defined as the distance between the projection of the central metal onto the C_5B plane and the geometric center of the C_5B ring.

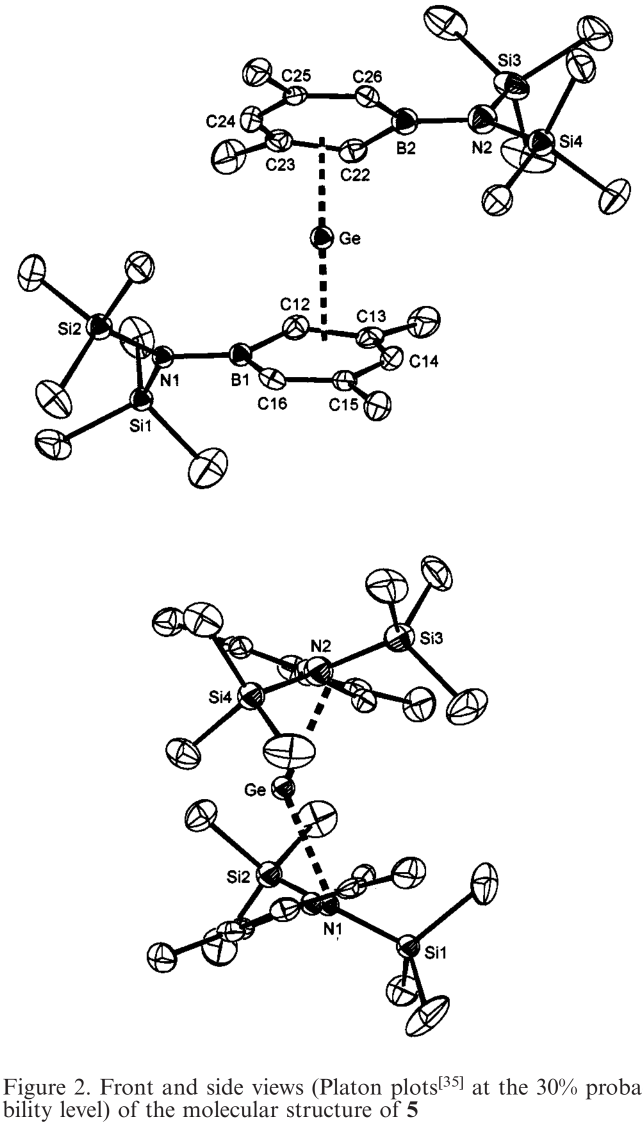

Figure 2. Front and side views (Platon plots[35] at the 30% probability level) of the molecular structure of **5**

The slip distortions, defined as the distances between the projections of the central metals onto the ligand C_5B planes and the geometric centers of the C_5B rings, are 0.56 Å for **5**, 0.51 Å for **6**, and 0.43 Å for **7** on average. These slip distortions are essentially directed toward one of the two ortho-carbon atoms (C*n*2), as can readily be seen from the extremely short E−C*n*2 and at the same time rather long E−C*n*6 distances. The rings also display substantial deviations from planarity. In all cases, the C*n*2 atoms show the largest vertical displacements [0.043−0.056 Å] from the best C_5B planes and toward the central elements.

The π-electron distribution of the boratabenzene ring and the intra-ring B−C bond polarization concentrate negative charge onto the α-carbons.[19−21,25] A symmetric slip toward the boron atom would indicate a largely ionic interaction as in the case of $Mg(C_5H_5BMe)_2$.[25] On the other hand, the combination of an asymmetric slip toward one of the two α-carbon atoms with a partial localization of the ring π-electron system would be expected in cases with significant covalent orbital interactions, as for instance for 2-$(Me_3Sn)C_5H_5BMe$.[20] The Ge compound **5** displays the most asymmetric coordination of the central atom, and the intra-ring bond lengths [cf. B1−C12 1.515(7), C12−C13 1.428(6), C13−C14 1.388(6), C14−C15 1.411(6), C15−C16 1.374(6), B1−C16 1.523(6) Å] show some localization of the π-electron system. The situation is still far from a fully localized diene system, but we may safely conclude that covalent orbital interactions contribute significantly to the bonding in this case. On the other hand, the Pb compound **7** shows a less asymmetric slip, and the intra-ring distances [cf. B1−C12 1.532(10), C12−C13 1.403(9), C13−C14 1.396(10), C14−C15 1.400(10), C15−C16 1.385(9), B1−C16 1.514(10) Å] show barely significant differences which exclude any pronounced localization of the π-electron system. Hence electrostatic interactions are more important in this case.

The tilt angles of the sandwich units are remarkably large in all three structures. For instance, an averaged interplanar angle of 51° is found for the lead compound **7**. In comparison, the sterically less demanding compound bis(1-methylboratabenzene)lead (**3**) possesses a smaller tilt angle of 44° despite the marked short intermolecular interactions in the structure.[19] Although it is generally accepted that steric congestion may cause a decrease of the bending angle of the group 14 sandwich compounds, a rationalization of the molecular geometries based solely on this line seems insufficient. Recent ab initio calculations on the parent stannocene and plumbocene predict very small energy gaps between the bent and linear forms.[36] In addition, accumulating experimental evidence tends to support the notion that the molecular shapes of this family of compounds are strongly affected by lattice forces, as one would expect for soft structural parameters. A pertinent example is the fact that decaisopropylplumbocene $Pb(C_5Pri_5)_2$ [10a] is bent, whereas the less highly substituted hexaisopropyl analogue $Pb(C_5H_2Pri_3)_2$ [15] is linear.

Concluding Remarks

This paper presents work on bis(aminoboratabenzene) compounds of divalent group 14 elements. We found that the thermal stability of the plumbocene analogues decreases in the order **3** > **7** > **4**. This sequence parallels the basicity of the corresponding boratabenzene ligands and suggests that the stability is tunable by varying the *B*-bonded groups.

Crystal structure analyses reveal a monomeric bent-sandwich structure for the compounds **5**−**7**. The molecules possess rather large tilt angles, implying that the bulky substituents of the ligands do not necessarily result in less bent molecular geometries for group 14 metallocenes. In all three structures, the metal−ligand bonding is surprisingly asymmetric with large slip distortions. This observation, together with the synopsis of the ^{11}B NMR spectroscopic data, suggests that the metal−ligand interactions comprise large electrostatic contributions for this family of compounds which increase on going from Ge to Pb.

Experimental Section

General: All manipulations were carried out under an inert atmosphere of nitrogen by means of standard Schlenk techniques. Pentane was distilled from Na/K alloy, toluene from sodium, and Et_2O from sodium benzophenone ketyl solution. Anhydrous GeI_2, $SnCl_2$, and PbI_2 were used as received from commercial sources. The lithium salts $Li(3,5\text{-}Me_2C_5H_3BNMe_2)$[29,37] and $Li[3,5\text{-}Me_2C_5H_3BN(SiMe_3)_2]$[29] were prepared according to established procedures. Electron-impact mass spectra were recorded on a Finnigan MAT-95 at a nominal electron energy of 70 eV. Elemental analyses were performed at the Analytische Laboratorien, 51779 Lindlar, Germany.

NMR spectra were recorded on a Varian Unity 500 (^1H: 500 MHz; ^{13}C: 125.7 MHz; ^{11}B: 160.4 MHz; ^{119}Sn: 186.5 MHz; ^{207}Pb: 104.6 MHz), a Varian Mercury 200 (^1H: 200 MHz; ^{13}C: 50.3 MHz), or a PMR Firenze spectrometer (^{11}B: 27.9 MHz). Chemical shifts are given in ppm and are referenced to TMS for ^1H and ^{13}C, to $BF_3{\cdot}OEt_2$ for ^{11}B, to $SnMe_4$ for ^{119}Sn, and to $PbMe_4$ for ^{207}Pb. In the case of ^{207}Pb, a solution of $PbEt_4$ (17%, $\delta = 74.8$)[38] in CD_2Cl_2 was used as external standard.

Synthesis of Bis(1-dimethylamino-3,5-dimethylboratabenzene)lead (4): $Li(3,5\text{-}Me_2C_5H_3BNMe_2)$ (0.53 g, 3.42 mmol) in ether (10 mL) was added to a suspension of $PbCl_2$ (0.48 g, 1.71 mmol) in ether (10 mL) at −30 °C. The reaction mixture was stirred at this temperature for 24 h to give a red solution. After removal of the solvent under high vacuum at −30 °C, cold pentane (15 mL, −78 °C) was injected to the residue and a precipitate of LiCl was filtered off quickly. All the solvent was pumped off from the filtrate to give **4** (ca. 0.6 g, 70%) as a red oil that can be stored at −78 °C for weeks. Upon standing at room temperature, compound **4** decomposes to give lead black and a pale yellow oil; this oil contains the ligand-coupling products and consists mainly (ca. 80%) of the 4,4′-isomer.

Data for 4: ^1H NMR (200 MHz, $CDCl_3$, −20 °C): $\delta = 2.10$ (s, 2 × 3-/5-Me), 2.90 (s, 2 × NMe_2), 4.97 (s, 2 × 2-/6-H), 6.10 (s, 2 × 4-H). − $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, −20 °C): $\delta = 24.3$ (3-/5-Me), 39.0 (NMe_2), 109.3 (C-4), 114.1 (br, C-2,6), 148.5 (C-3,5). − ^{11}B NMR (28 MHz, $CDCl_3$, external $BF_3{\cdot}OEt_2$, −20 °C): $\delta = 32$.

Data for the 4,4′-Isomeric Ligand-coupling Product: ^1H NMR (200 MHz, $CDCl_3$, 20 °C): $\delta = 1.91$ (s, 3-/3′-/5-/5′-Me), 2.83 (s, 2 × NMe_2), 3.23 (s, 4-/4′-H), 5.96 (s, 2-/2′-/6-/6′-H). − $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 20 °C): $\delta = 26.6$ (3-/5-Me), 39.1 (NMe_2), 52.5 (C-4,4′), 127.0 (br, C-2,2′,6,6′), 159.2 (C-3,3′,5,5′).

Synthesis of Bis[1-bis(trimethylsilyl)amino-3,5-dimethylboratabenzene]germanium (5): $Li[3,5\text{-}Me_2C_5H_3BN(NSiMe_3)_2]$ (0.64 g, 2.36 mmol) in ether (10 mL) was added dropwise to GeI_2 (0.39 g, 1.18 mmol) in ether (10 mL) at 0 °C. The system was allowed to warm to ambient temperature and stirring was continued for 6 h to give a yellow slurry. After the solvent had been completely removed under vacuum, pentane (30 mL) was added to the residue. A white precipitate of LiCl was removed by filtration and washed with pentane (2 × 5 mL). The combined filtrate was concentrated and cooled to −30 °C for 3 days to give **5** (0.52 g, 73%) as pale yellow crystals. The compound is extremely sensitive to moisture and air.

Data for 5: ^1H NMR (500 MHz, CD_2Cl_2, 20 °C): $\delta = 0.20$ (s, 4 $SiMe_3$), 2.06 (s, 2 × 3-/5-Me), 5.32 (t, $J = 1.5$ Hz, 2 H, 4-H), 5.44 (d, $J = 1.5$ Hz, 2 × 2-/6-H). − $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 20 °C): $\delta = 4.7$ ($SiMe_3$), 25.1 (3-/5-Me), 117.9 (C-4), 122.0 (br, C-2,6), 147.8 (C-3,5). − ^{11}B NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}OEt_2$, 20 °C): $\delta = 37.8$. − $C_{26}H_{54}B_2GeN_2Si_4$ (601.3): calcd. C 51.94, H 9.05, N 4.66; found C 51.69, H 9.23, N 4.55.

Synthesis of Bis[1-bis(trimethylsilyl)amino-3,5-dimethylboratabenzene]tin (6): $Li[3,5\text{-}Me_2C_5H_3BN(NSiMe_3)_2]$ (231 mg, 0.85 mmol) in ether (10 mL) was added dropwise to $SnCl_2$ (80 mg, 0.42 mmol) in ether (5 mL) at 0 °C. The system was allowed to warm to ambient temperature and stirring was continued for 6 h to give a yellow slurry. After the solvent had been completely removed under vacuum, pentane (20 mL) was added to the residue. A white precipitate of LiCl was removed by filtration and washed with pentane (5 mL). The combined filtrate was concentrated and cooled to −30 °C overnight to give **6** (0.17 g, 63%) as pale yellow crystals. The compound is sensitive to moisture and air.

Data for 6: ^1H NMR (500 MHz, CD_2Cl_2, 20 °C): $\delta = 0.21$ (s, 4 × $SiMe_3$), 2.10 (s, 2 × 3-/5-Me), 5.32 (t, $J = 1.2$ Hz, 2 × 4-H), 5.51 (d, $J = 1.2$ Hz, 2 × 2-/6-H). − $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 20 °C): $\delta = 4.9$ ($SiMe_3$), 24.9 (3-/5-Me), 113.7 (C-4), 123.8 (br, C-2,6), 148.1 (C-3,5). − ^{11}B NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}OEt_2$, 20 °C): $\delta = 36.3$. − ^{119}Sn NMR (186 MHz, CD_2Cl_2, external $SnMe_4$, 20 °C): $\delta = -1592$. − $C_{26}H_{54}B_2N_2Si_4Sn$ (647.4): calcd. C 48.24, H 8.41, N 4.33; found C 48.14, H 8.40, N 4.17.

Synthesis of Bis[1-bis(trimethylsilyl)amino-3,5-dimethylboratabenzene]lead (7): $Li[3,5\text{-}Me_2C_5H_3BN(NSiMe_3)_2]$ (0.56 g, 2.06 mmol) in ether (20 mL) was added dropwise to a suspension of $PbCl_2$ (0.28 g, 1.02 mmol) in ether (10 mL) at −78 °C. The system was allowed to warm to ambient temperature and stirring was continued for 6 h to give an orange slurry. After the solvent had been completely removed under vacuum, pentane (30 mL) was added to the residue. A white precipitate of LiCl was removed by filtration and washed with pentane (2 × 5 mL). The combined filtrate was concentrated to ca. 5 mL and cooled to −30 °C to afford **7** (0.64 g, 85%) as large orange-red crystalline blocks which are sensitive to moisture and air.

Table 6. Crystal data, data collection parameters, and convergence results for **5**−**7**

	5	**6**	**7**
Empirical formula	$C_{26}H_{54}B_2GeN_2Si_4$	$C_{26}H_{54}B_2N_2Si_4Sn$	$C_{26}H_{54}B_2N_2PbSi_4$
Molecular weight	601.28	647.39	735.89
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a [Å]	10.877(2)	14.806(5)	14.913(4)
b [Å]	27.330(8)	15.345(4)	15.394(3)
c [Å]	12.178(4)	16.060(3)	16.036(3)
α [deg]		89.54(3)	89.57(2)
β [deg]	96.13(2)	103.49(3)	103.45(2)
γ [deg]		90.41(2)	90.36(2)
V [Å^3]	3599(2)	3548(2)	3580(1)
Z	4	4	4
$d_{calcd.}$ [g/cm^3]	1.11	1.21	1.37
$F(000)$	1288	1360	1488
μ [cm^{-1}]	9.86	8.71	48.94
Absorption correction	empirical	none	empirical
Max./min. transmission	0.998/0.943		1.000/0.417
θ range [deg]	3.0−26.0	3.0−25.0	3.0−26.0
Temperature [K]	223	213	233
Crystal size [mm]	0.60 × 0.50 × 0.45	0.30 × 0.30 × 0.25	0.40 × 0.34 × 0.18
Reflections collected	10206	16361	15020
Reflections unique	7021 (R_{int} = 0.079)	12415 (R_{int} = 0.068)	13984(R_{int} = 0.030)
Reflections observed	3994	5956	8016
Criterion for observation	$I > 2\,\sigma(I)$	$I > 2\,\sigma(I)$	$I > 2\,\sigma(I)$
Variables	332	663	663
R_1,[a] observed (all data)	0.058 (0.131)	0.070 (0.164)	0.040 (0.089)
wR_2,[b] observed (all data)	0.111 (0.128)	0.137 (0.161)	0.085 (0.093)
GOF[c]	0.923	0.898	0.923
Max. resd. density [e/Å^3]	0.53	1.12 (close to Sn)	2.03 (close to Pb)

[a] $R_1 = ||F_o| - |F_c||/|F_o|$. − [b] $wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. − [c] GOF = $[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$.

Data for 7: ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ = 0.20 (s, 4 $SiMe_3$), 2.19 (s, 2 × 3-/5-Me), 5.32 (t, J = 1.8 Hz, 2 × 4-H), 5.41 (d, J = 1.8 Hz, 2 × 2-/6-H). − ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 20 °C): δ = 5.0 ($SiMe_3$), 24.6 (3-/5-Me), 113.5 (C-4), 125.0 (br, C-2,6), 148.5 (C-3,5). − ^{11}B NMR (160 MHz, CD_2Cl_2, external BF_3·OEt_2, 20 °C): δ = 35.2. − ^{207}Pb NMR (105 MHz, CD_2Cl_2, external $PbEt_4$, relative to $PbMe_4$, 20 °C): δ = −2890. − $C_{26}H_{54}B_2N_2PbSi_4$ (735.9): calcd. C 42.44, H 7.40, N 3.81; found C 41.27, H 7.51, N 3.72.

X-ray Crystal Structure Determinations of 5−7: Data collection was performed on an ENRAF-Nonius CAD4 diffractometer with Mo-K_α radiation (graphite monochromator, λ = 0.71073 Å) using the ω-2θ scan mode. Crystal data, data collection parameters, and convergence results are listed in Table 6. Empirical absorption corrections on the basis of azimuthal scans[39] were applied to the data sets of **5** and **7** before merging symmetry-related reflections. The structure of **5** was solved by direct methods whereas the solutions for compounds **6** and **7** were obtained by conventional heavy atom methods.[40] All three structures were refined on reflection intensities (F^2) with the SHELXL-97 program.41] In the final structural models, non-hydrogen atoms were refined with the anisotropic displacement parameters while hydrogen atoms were included as riding with fixed displacement parameters [C−H = 0.98 Å, U_{iso}(H) = 1.3 U_{eq}(C)].[42]

Acknowledgments

We thank Dr. U. Englert for helpful advice with the X-ray structure determinations. This work was generously supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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[1] [1a] P. Jutzi, N. Burford, *Chem. Rev.* **1999**, *99*, 969−990. − [1b] P. Jutzi, N. Burford, in *Metallocenes*, vol. 1 (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, Germany, **1998**, p. 3−54. − [1c] P. Jutzi, *J. Organomet. Chem.* **1990**, *400*, 1−17. − [1d] P. Jutzi, *Adv. Organomet. Chem.* **1986**, *26*, 217−295.

[2] [2a] M. A. Beswick, J. S. Palmer, D. S. Wright, *Chem. Soc. Rev.* **1998**, *27*, 225−232. − [2b] M. A. Beswick, H. Gornitzka, J. Kärcher, M. E. G. Mosquera, J. S. Palmer, P. R. Raithby, C. A. Russel, D. Stalke, A. Steiner, D. S. Wright, *Organometallics* **1999**, *18*, 1148−1153. − [2c] D. R. Armstrong, M. J. Duer, M. G. Davidson, D. Moncrieff, C. A. Russell, C. Stourton, A. Steiner, D. Stalke, D. S. Wright, *Organometallics* **1997**, *16*, 3340−3351. − [2d] M. A. Beswick, N. L. Cromhout, C. N. Harmer, P. R. Raithby, C. A. Russel, J. S. B. Smith, A. Steiner, D. S. Wright, *Chem. Commun.* **1996**, 1977−1978.

[3] [3a] J. Satgé, P. Rivière, M. Rivière-Baudet, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), vol. 2 (volume Ed.: A. G. Davies), Pergamon Press, Oxford, U. K., **1995**, p. 137−216. − [3b] A. G. Davies, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel,

F. G. A. Stone, G. Wilkinson), vol. 2 (volume Ed.: A. G. Davies), Pergamon Press, Oxford, U. K., **1995**, p. 217−303. − [3c] P. G. Harrison, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), vol. 2 (volume Ed.: A. G. Davies), Pergamon Press, Oxford, U. K., **1995**, p. 305−319.

[4] [4a] J. S. Overby, T. P. Hanusa, V. G. Young, Jr., *Inorg. Chem.* **1998**, *37*, 163−165. − [4b] C. Panattoni, G. Bombieri, U. Croatto, *Acta Crystallogr.* **1966**, *21*, 823−826.

[5] M. A. Beswick, C. Lopez-Casideo, M. A. Paver, P. R. Raithby, C. A. Russell, A. Steiner, D. S. Wright, *Chem. Commun.* **1997**, 109−110.

[6] [6a] J. V. Scibelli, M. D. Curtis, *J. Am. Chem. Soc.* **1973**, *95*, 924−925. − [6b] M. Grenz, E. Hahn, W.-W. du Mont, J. Pickardt, *Angew. Chem.* **1984**, *96*, 69−70; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 61.

[7] [7a] E. O. Fischer, H. Grubert, *Z. Naturforsch., Teil B* **1956**, *11*, 423−424. − [7b] J. L. Atwood, W. E. Hunter, A. H. Cowley, R. A. Jones, C. A. Stewart, *J. Chem. Soc., Chem. Commun.* **1981**, 925−927.

[8] [8a] A. H. Cowley, P. Jutzi, F. X. Kohl, J. G. Lasch, N. C. Norman, E. Schlüter, *Angew. Chem.* **1984**, *96*, 603−604; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 616. − [8b] P. Jutzi, B. Hielscher, *Organometallics* **1986**, *5*, 1201−1204. − [8c] P. Jutzi, E. Schlüter, M. B. Hursthouse, A. M. Arif, R. L. Short, *J. Organomet. Chem.* **1986**, *299*, 285−295.

[9] [9a] H. Schumann, C. Janiak, E. Hahn, J. Loebel, J. J. Zuckerman, *Angew. Chem.* **1985**, *97*, 765; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 773. − [9b] H. Schumann, C. Janiak, E. Hahn, C. Kolax, J. Loebel, M. D. Rausch, J. J. Zuckerman, M. J. Heeg, *Chem. Ber.* **1986**, *119*, 2656−2667.

[10] [10a] H. Sitzmann, *Z. Anorg. Allg. Chem.* **1995**, *621*, 553−556. − [10b] D. J. Burkey, T. P. Hanusa, *Organometallics* **1995**, *14*, 11−13. − [10c] W. W. Schoeller, O. Friedrich, A. Sundermann, A. Rozhenko, *Organometallics* **1999**, *18*, 2099−2106.

[11] W. J. Evans, R. D. Clark, K. J. Forrestal, J. W. Ziller, *Organometallics* **1999**, *18*, 2401−2402.

[12] M. J. Heeg, C. Janiak, J. J. Zuckerman, *J. Am. Chem. Soc.* **1984**, *106*, 4259−4261.

[13] [13a] S. P. Constantine, P. B. Hitchcock, G. A. Lawless, G. M. de Lima, *Chem. Commun.* **1996**, 1101−1102. − [13b] S. P. Constantine, P. B. Hitchcock, G. A. Lawless, *Organometallics* **1996**, *15*, 3905−3906. − [13c] S. P. Constantine, H. Cox, P. B. Hitchcock, G. A. Lawless, *Organometallics* **2000**, *19*, 317−326.

[14] H. Sitzmann, R. Boese, P. Stellberg, *Z. Anorg. Allg. Chem.* **1996**, *622*, 751−755.

[15] D. J. Burkey, T. P. Hanusa, J. C. Huffman, *Inorg. Chem.* **2000**, *39*, 153−155.

[16] T. J. Lee, J. E. Rice, *J. Am. Chem. Soc.* **1989**, *111*, 2011−2017.

[17] For reviews on borabenzene chemistry, see: [17a] G. E. Herberich, in *Advances in Boron Chemistry* (Ed.: W. Siebert), The Royal Society of Chemistry, Cambridge, U. K., **1997**, Special Publication No. 201, p. 211−223. − [17b] G. E. Herberich, H. Ohst, *Adv. Organomet. Chem.* **1986**, *25*, 199−236. − [17c] A. J. Ashe III, S. Al-Ahmad, X. Fang, *J. Organomet. Chem.* **1999**, *581*, 92−97.

[18] For further leading references on borabenzene chemistry, see: [18a] A. J. Ashe III, S. Al-Ahmad, X. Fang, J. W. Kampf, *Organometallics* **2001**, *20*, 468−473. − [18b] D. H. Woodmansee, X. Bu, G. Bazan, *Chem. Commun.* **2001**, 619−620. − [18c] X. Zheng, G. E. Herberich, *Organometallics* **2000**, *19*, 3751−3753.

[19] G. E. Herberich, X. Zheng, J. Rosenplänter, U. Englert, *Organometallics* **1999**, *18*, 4747−4752.

[20] G. E. Herberich, J. Rosenplänter, B. Schmidt, U. Englert, *Organometallics* **1997**, *16*, 926−931.

[21] U. Englert, G. E. Herberich, J. Rosenplänter, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1098−1102.

[22] G. E. Herberich, H. J. Becker, C. Engelke, *J. Organomet. Chem.* **1978**, *153*, 265−270.

[23] G. E. Herberich, U. Englert, B. Ganter, M. Pons, R. Wang, *Organometallics* **1999**, *18*, 3406−3413.

[24] G. E. Herberich, B. Schmidt, U. Englert, T. Wagner, *Organometallics* **1993**, *12*, 2891−2893.

[25] X. Zheng, U. Englert, G. E. Herberich, J. Rosenplänter, *Inorg. Chem.* **2000**, *39*, 5579−5585.

[26] A. J. Ashe III, J. W. Kampf, C. Müller, M. Schneider, *Organometallics* **1996**, *15*, 387−393.

[27] G. C. Bazan, W. D. Cotter, Z. J. A. Komon, R. A. Lee, R. J. Lachicotte, *J. Am. Chem. Soc.* **2000**, *122*, 1371−1380.

[28] F. G. Bordwell, *Acc. Chem. Res.* **1988**, *21*, 456−463.

[29] G. E. Herberich, U. Englert, A. Fischer, J. Ni, A. Schmitz, *Organometallics* **1999**, *18*, 5496−5501.

[30] G. E. Herberich, B. Schmidt, U. Englert, *Organometallics* **1995**, *14*, 471−480.

[31] R. K. Harris, J. D. Kennedy, W. McFarlane, in *NMR and the Periodic Table* (Eds.: R. K. Harris, B. E. Mann), Academic Press, London, U. K., **1978**, p. 351.

[32] C. Janiak, H. Schumann, C. Stader, B. Wrackmeyer, J. J. Zuckerman, *Chem. Ber.* **1988**, *121*, 1745−1751.

[33] P. Jutzi, B. Hielscher, *J. Organomet. Chem.* **1985**, *291*, C25−C27.

[34] [34a] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73−186. − [34b] B. Wrackmeyer, K. Horchler, *Annu. Rep. NMR Spectrosc.* **1990**, *22*, 249−306. − [34c] B. Wrackmeyer, A. Sebald, L. H. Merwin, *Magn. Reson. Chem.* **1991**, *29*, 260−263.

[35] A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

[36] D. R. Armstrong, M. A. Beswick, N. L. Cromhout, C. N. Harmer, D. Moncrieff, C. A. Russell, P. R. Raithby, A. Steiner, A. E. H. Wheatley, D. S. Wright, *Organometallics* **1998**, *17*, 3176−3181.

[37] G. E. Herberich, U. Englert, M. U. Schmidt, R. Standt, *Organometallics* **1996**, *15*, 2707−2712.

[38] J. D. Kennnedy, W. McFarlane, G. S. Pyne, *J. Chem. Soc., Dalton Trans.* **1977**, 2332−2339.

[39] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351−359.

[40] G. M. Sheldrick, *SHELXS-97, Program for Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.

[41] G. M. Sheldrick, *SHELXL-97, Program for Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

[42] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-164368 (**5**), CCDC-164369 (**6**), and CCDC-164370 (**7**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received June 1, 2001
[I01201]